

University of Groningen

## Optical Nuclear Polarization in the Excited State Through Cross-Relaxation and Its Use in the Study of the Carbon-13 Hyperfine Coupling in the Lowest Triplet State of 1-<sup>13</sup>C-p-Benzoquinone

Lichtenbelt, Jan H.; Fremmeijer, Jan G.F.M.; Wiersma, Douwe A.

*Published in:*  
Chemical Physics

*DOI:*  
[10.1016/0301-0104\(76\)87039-5](https://doi.org/10.1016/0301-0104(76)87039-5)

**IMPORTANT NOTE:** You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1976

[Link to publication in University of Groningen/UMCG research database](#)

### *Citation for published version (APA):*

Lichtenbelt, J. H., Fremmeijer, J. G. F. M., & Wiersma, D. A. (1976). Optical Nuclear Polarization in the Excited State Through Cross-Relaxation and Its Use in the Study of the Carbon-13 Hyperfine Coupling in the Lowest Triplet State of 1-<sup>13</sup>C-p-Benzoquinone. *Chemical Physics*, 18(1). [https://doi.org/10.1016/0301-0104\(76\)87039-5](https://doi.org/10.1016/0301-0104(76)87039-5)

### **Copyright**

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### **Take-down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

## OPTICAL NUCLEAR POLARIZATION IN THE EXCITED STATE THROUGH CROSS-RELAXATION AND ITS USE IN THE STUDY OF THE CARBON-13 HYPERFINE COUPLING IN THE LOWEST TRIPLET STATE OF 1-<sup>13</sup>C-*p*-BENZOQUINONE

Jan H. LICHTENBELT, Jan G.F.M. FREMEIJER and Douwe A. WIERSMA

*Laboratory for Physical Chemistry, University of Groningen,  
Zernikelaan, Paddepoel, Groningen, The Netherlands*

Received 28 May 1976

In this paper the phenomenon of optical nuclear polarization in the excited state through cross-relaxation is described. It is shown that when the populating and depopulating rates of the triplet spin sublevels are known the absolute nuclear polarizations can be calculated and that optical detection of the nuclear alignment in at least one electron spin state is quite often feasible.

The paper further deals with the magnetic resonance properties of the lowest triplet state in 1-<sup>13</sup>C-*p*-benzoquinone where of the zero-field splitting parameters and carbon-13 hyperfine data are reported. The carbon-13 hyperfine data, obtained by optical detection of ENDOR and CRENDOR, indicate that in the lowest  $\pi\pi^*$  triplet state of *p*-benzoquinone the  $\pi$ -electron spin density at the carbonyl carbon and oxygen are about equal while the remaining carbon atoms carry about half this spin density.

### 1. Introduction

The phenomenon of nuclear spin polarization in the ground state through optical pumping has been the subject of several studies in the past decade [1]. The effect originates from the combination of electron spin-selective intersystem crossing and hyperfine interaction.

The presence of nuclear spin alignment in triplet excited states is naturally of great interest as it may enable us to detect nuclear transitions with greatly enhanced sensitivity.

In a previous paper [2] we showed that a very high degree of nuclear spin polarization can be achieved at the cross-relaxation magnetic field of a triplet excited molecule and a doublet spin system. In the present paper we describe and analyze this effect in greater detail.

We further report usage of the effect to obtain the hyperfine coupling tensor of the carbonyl <sup>13</sup>C nucleus in the lowest triplet state of 1-<sup>13</sup>C-*p*-benzoquinone-*h*<sub>4</sub> and discuss the implications of this measurement towards the geometry of and spin density distribution in this state of the molecule.

### 2. Nuclear spin polarization through cross-relaxation

Veeman et al. [3,4] recently described and analyzed in detail the level anticrossing (LAC) and cross-relaxation (CR) effects that occur in phosphorescent organic crystals.

One of the conclusions reached was that these effects might possibly be used to achieve nuclear spin alignment in triplet excited states of molecules.

In the course of our EPR and ENDOR experiments on the lowest triplet state of PBQ [2] we found clear evidence that at least CR produces a high degree of nuclear spin polarization.

This nuclear alignment was optically detected through observation of radio frequency induced changes of the phosphorescence cross-relaxation signal and this new technique was named CRENDOR, an acronym for cross relaxation nuclear double resonance. In this note we will further analyze the cross-relaxation effect at 1.8 K between a triplet excited *p*-benzoquinone-carbonyl-<sup>13</sup>C (1-<sup>13</sup>C-PBQ-*h*<sub>4</sub>) molecule and a photochemically produced radical both as guests in a PBQ-*d*<sub>4</sub> host lattice.

For the moment we will only consider the <sup>13</sup>C nuclear spin in the triplet state and a doublet electron-spin sys-

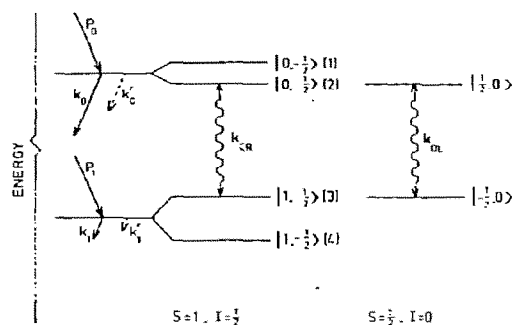


Fig. 1. Energy level scheme at cross-relaxation of a system consisting out of a triplet state spin system with a nuclear spin  $\frac{1}{2}$  ( $S = 1, I = \frac{1}{2}$ ) and a doublet spin system ( $S = \frac{1}{2}, I = 0$ ) for a magnetic field along the fine-structure z-axis. Note that  $D$  is negative.  $P$  stands for populating rate,  $k$  for total decay rate,  $k^r$  for radiative decay rate,  $k_{cr}$  for cross-relaxation rate and  $k_{dl}$  for spin-lattice relaxation rate.

tem without nuclear spins. This model is realistic in the sense that in the doublet electron-spin system no nuclear alignment is observed (vide infra).

For a magnetic field parallel to the principal z-axis of the fine-structure tensor, which coincides with the long molecular (z) axis of 1- $^{13}\text{C}$ -PBQ- $h_4$ , the cross-relaxation situation sketched in fig. 1 is reached at a magnetic field of  $\sim 386$  gauss.

First consider the situation outside the crossing region, where the two spin systems are uncoupled.

As spin-lattice relaxation at 1.8 K among the triplet spin components is slow compared to all decay constants [2], the steady state populations  $N_0$  and  $N_1$  of the  $|0\rangle$  and  $|+1\rangle$  triplet spin sublevels are only determined by the populating ( $P$ ) and decay ( $k$ ) rates as follows:

$$N_0/N_1 = P_0 k_1 / P_1 k_0. \quad (1)$$

In the specific case of PBQ the populating rates are unknown, but as feeding of the triplet spin system occurs via the host exciton band, we imagine that  $P_0$  and  $P_1$  are almost identical, which implies [5] that

$$N_0/N_1 = k_1/k_0 = \frac{1}{2}(k_x + k_y)/k_z = \frac{1}{3}.$$

Outside the crossing region the electron spin system thus is strongly polarized. Note however that the ratio  $P_0 k_1 / P_1 k_0$  is dependent of the magnetic field orientation and this directly determines the maximum attainable electron spin polarization.

The spin system of the stable photochemically produced radical is outside the crossing region most likely in Boltzmann equilibrium with the lattice.

When the two spin systems are brought into contact with each other at the cross-relaxation field then what happens depends on the relative magnitudes of the different rate constants of the coupled systems. Veeman et al. [4] showed that when cross-relaxation is described as a contact between heat reservoirs of different temperatures, a permanent change of the phosphorescence intensity due to CR, as observed in PBQ, only occurs if the following inequality holds:

$$k_1 < k_{cr} < k_{dl}.$$

Herein  $k_1$  is the decay rate of the  $|+1\rangle$  triplet state level,  $k_{cr}$  the CR rate between the triplet and doublet spin system and  $k_{dl}$  the spin-lattice relaxation rate of the doublet spin system. In this case CR effectively induces spin-lattice relaxation among the triplet spin sublevels.

This process however is only nuclear spin selective when also the following relation holds:  $k_{cr} < 2\pi\Delta\nu_N$ ; whereby  $\Delta\nu_N$  is the energy difference between the nuclear spin states of the same electron spin level. This inequality assures that the nuclear spinstates are not within the uncertainty energy-width of the cross-relaxation process. In only that case, and assuming slow nuclear spin-lattice relaxation, we succeed in converting the electron spin polarization into nuclear polarization. With reference to fig. 1 we calculate (ignoring the Boltzmann factor) for the steady state populations of the different hyperfine levels at low temperature:

$$N_1 = P_0/k_0, \quad (2a)$$

$$N_2 = [k_1 P_0 + k_{cr}(P_0 + P_1)] / [k_1 k_0 + k_{cr}(k_0 + k_1)], \quad (2b)$$

$$N_3 = [k_0 P_1 + k_{cr}(P_0 + P_1)] / [k_1 k_0 + k_{cr}(k_0 + k_1)], \quad (2c)$$

$$N_4 = P_1/k_1. \quad (2d)$$

When  $k_{cr} \gg k_1, k_0$  one calculates for the phosphorescence intensity change induced by CR from eqs. (2):

$$\Delta I = [(P_0 + P_1)/(k_0 + k_1)] (k_0^r + k_1^r) - (P_0/k_0) k_0^r - (P_1/k_1) k_1^r, \quad (3)$$

whereby  $k_0^r$  and  $k_1^r$  are the radiative constants of the  $|0\rangle$  and  $|+1\rangle$  spin sublevels.

For PBQ it is further known [5] that  $k_0 \gg k_1$  which

implies that  $\Delta I$  becomes:

$$\Delta I = P_1 \left( \frac{k_0^T + k_1^T (1 + P_0/P_1)}{k_0} - \frac{k_1^T}{k_1} \right). \quad (4)$$

Under the same condition  $k_{cr} \gg k_0, k_1$  we calculate for the absolute nuclear polarization (ANP) defined as  $|N_i - N_j|/(N_i + N_j)$ , in the  $|0\rangle$  and  $|+1\rangle$  electron spin level respectively the following:

$$|k_0 P_1 - k_1 P_0| / [k_0 (2P_0 + P_1) + k_1 P_0] \quad (5a)$$

and

$$|k_0 P_1 - k_1 P_0| / [k_1 (2P_1 + P_0) + k_0 P_1]. \quad (5b)$$

For a magnetic field along the fine-structure z-axis of PBQ and assuming  $P_0 = P_1$  we find, using the fact that  $k_1/k_0 = \frac{1}{30}$ :

$$\text{ANP}_{|0\rangle} = 29/91 \quad \text{and} \quad \text{ANP}_{|+1\rangle} = 29/33.$$

CR in the case of PBQ thus produces a high degree of nuclear spin polarization especially in the  $|+1\rangle$  electron spin level for a magnetic field parallel z.

This nuclear spin alignment was previously detected [2] through observation of radio frequency induced changes in the CR effect of PBQ and we will now proceed by calculating the expected change of the CR effect. Consider therefore the effect of a strong rf field that is resonant with a nuclear transition in the  $|+1\rangle$  electron spin state. CR then effectively occurs between the levels 2 and 3,4 of fig. 1 and produces a change in the steady state populations. Assuming again  $k_{cr}$  to greatly exceed  $k_0$  and  $k_1$  we calculate in this situation the following steady state populations:

$$N_1 = P_0/k_0, \quad (6a)$$

$$N_2 = N_3 = N_4 = (P_0 + 2P_1)/(k_0 + 2k_1). \quad (6b)$$

The phosphorescence intensity change of the CRENDOR effect is then calculated to be:

$$\Delta I = [(P_0 + 2P_1)/(k_0 + 2k_1)] (k_0^T + 2k_1^T) - [(P_0 + P_1)/(k_0 + k_1)] (k_0^T + k_1^T) - (P_1/k_1) k_1^T. \quad (7)$$

Utilizing the fact that  $k_0 \gg k_1$  in PBQ  $\Delta I$  is found to be:

$$\Delta I = P_1 \left( \frac{k_0^T + k_1^T (3 + P_0/P_1)}{k_0} - \frac{k_1^T}{k_1} \right). \quad (8)$$

Comparison of this expression with eq. (4) shows that the CRENDOR effect in the  $|+1\rangle$  electron spin state even exceeds the CR effect. Using the same approximations we calculate for the CRENDOR effect in the  $|0\rangle$  electron spin state:

$$\Delta I = -P_1 k_1^T / 2k_0. \quad (9)$$

It is interesting to note here that, despite considerable effort, we have so far only been able to detect these CRENDOR transitions in the  $|+1\rangle$  electron spin state of PBQ.

This could be due to either a negligible value of  $\Delta I$  in (9) or to the fact that the relation  $k_{cr} < 2\pi\Delta\nu_N$  no longer holds. Unfortunately in the case of PBQ the radiative rate constants are unknown so we cannot decide in this matter.

So far in the analysis of the CRENDOR effect we have assumed that the relation  $k_{cr} \gg k_0, k_1$  holds. As yet we have not been able to verify this, but an upper estimate of  $k_{cr}$  may be obtained from our CRENDOR spectra where the lowest observed transition is found at 6 MHz. This ascertains that  $k_{cr} < 2\pi \times 6 \text{ MHz}$ . As  $k_{cr}$  is directly related to the intermolecular interaction between the cross-relaxing species one expects of course a whole range of  $k_{cr}$  values. As shown in fig. 3, we indeed observe a change in the phosphorescence intensity of PBQ crystals in a magnetic field from zero up to  $\sim 760$  gauss and the "sharp" CR resonance on this broad feature then must be due to CR between a triplet species and specific non-neighbour doublet spin-systems. The quoted upper limit for  $k_{cr}$  and the nuclear spin polarizations calculated thus only refer to the "sharp" CR signal at 386 gauss in fig. 3. So far we have not concerned ourselves with the effect of cross-relaxation on possible nuclear spin polarization in the doublet spin system. Veeman et al. (4) showed that in order not to saturate the CR effect one demands  $k_{cr} \lesssim k_{dl}$  which results in a negligible nuclear polarization in the doublet species. In conclusion of this section we state that analysis of the CR effect shows that, knowing the populating and depopulation rates of a triplet spin system, one can easily calculate the induced absolute nuclear spin polarizations. The possibility of optical detection of this nuclear alignment however critically depends on the ratio between the radiative and non-radiative decay constants of the system.

### 3. Angular dependence of the cross-relaxation field

In PBQ, and most likely in many other molecules, the nuclear polarization induced by CR can be optically detected and used to obtain excited state hyperfine parameters.

To fully exploit the possibilities of this new CRENDOR technique the angular dependence of the cross-relaxation field needs to be known and in this section we therefore examine the energy-match between a triplet and doublet spin system in greater detail.

The energy of the triplet electron spin states is in first approximation determined by the spin hamiltonian:

$$\mathcal{H}_t = \beta_e \mathbf{H} \cdot \mathbf{g}_t \cdot \hat{\mathbf{S}} - (X\hat{S}_x^2 + Y\hat{S}_y^2 + Z\hat{S}_z^2), \quad (10)$$

whereby  $X$ ,  $Y$  and  $Z$  are the energies of the three spin sublevels in zero-field and the  $\mathbf{g}_t$  tensor in general is anisotropic. For the doublet spin-system the energies are determined by the Zeeman-term only:

$$\mathcal{H}_d = \beta_e \mathbf{H} \cdot \mathbf{g}_d \cdot \hat{\mathbf{S}}. \quad (11)$$

To match the energy difference in the doublet spin system with one of the energy gaps in the triplet spin system the following third degree polynomial in  $H^2$  determines the CR magnetic field:

$$\begin{aligned} & (\beta_e^2 H^2)^3 [(4g_t^2 - g_d^2)(g_t^2 - g_d^2)^2] \\ & - (\beta_e^2 H^2)^2 [3A(4g_t^2 - 2g_d^2)(g_t^2 - g_d^2) + 9F'^2] \\ & + (\beta_e^2 H^2) [3A^2(4g_t^2 - 3g_d^2) + 18BF'] \\ & - (4A^3 + 27B^2) = 0. \end{aligned} \quad (12)$$

In eq. (12) the following definitions have been used:

$$g_i = (\mathbf{I}^T \cdot \mathbf{g}_i \cdot \mathbf{g}_i^T \cdot \mathbf{I})^{1/2}, \quad i = t, d,$$

$$F' = \mathbf{I}^T \cdot \mathbf{g}_t \cdot \mathbf{F} \cdot \mathbf{g}_t^T \cdot \mathbf{I},$$

whereby  $\mathbf{F}$  is the fine structure tensor, with eigenvalues  $X$ ,  $Y$  and  $Z$ ;

$$\mathbf{H} = \mathbf{I}\mathbf{H},$$

with  $\mathbf{I}$  the unit magnetic field vector;

$$A = (XY + XZ + YZ), \quad B = (XYZ).$$

Note that  $\mathbf{g}_d$ ,  $\mathbf{g}_t$ ,  $\mathbf{F}$  and  $\mathbf{I}$  should be defined with respect to the same axis system.

For most organic molecules  $g_t \approx g_d$  which ensures that one root of eq. (12) will greatly exceed the other two. Physically this means that CR then occurs between Zeeman states, where the difference in  $g$ -values compensates for the zero-field splitting in the triplet spin system. However only the real root of eq. (12) at low magnetic fields is the physically interesting one and we now proceed by assuming that  $g_t = g_d$ . An analytic solution of this simplified equation can only be obtained if in addition we assume  $X = Y$ . In that case the cross-relaxation field ( $H_{cr}$ ) is calculated to be:

$$H_{cr} = \frac{1}{2g\beta_e} \left| \frac{Z}{3I_z^2 - 1} \right| [3(4I_z^2 - 1)]^{1/2}, \quad (13)$$

where  $I_z$  is the  $z$ -component of  $\mathbf{I}$  in the fine-structure axis system.

This expression for  $H_{cr}$  shows that  $H_{cr} \rightarrow \infty$  at the magic angle and that cross-relaxation no longer occurs when the angle between the magnetic field and the  $z$ -axis of the fine-structure-tensor exceeds  $60^\circ$ . Fig. 2 shows the angular dependence of the cross-relaxation

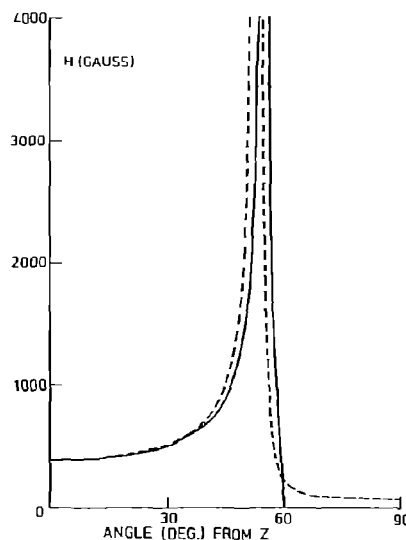


Fig. 2. Cross-relaxation field of a triplet-doublet spin system versus angle of rotation in the  $xz$  principal plane of the triplet state spin system. At zero degrees the magnetic field is along the  $z$ -axis of the fine-structure tensor. For the solid curve  $D = -2174$  MHz,  $E = 0$  and  $g_t = g_d = g_e$  while for the dashed curve  $g_d = g_e$  and for the triplet state species the fine structure and  $g$ -tensor values for 1-<sup>13</sup>C-PBQ-*H*<sub>4</sub> of table 1 were taken.

field in this simple case. In fig. 2 we have further included an example where  $X \neq Y \neq Z$  which requires numerical solution of eq. (12).

Finally it should be realized that at the low fields where CR occurs in these organic solids a first order solution of the CRENDOR transition frequency, as is customary in the treatment of the high field ENDOR data [6], is no longer warranted.

In the case of  $1^{13}\text{C-PBQ-}h_4$  we therefore extracted the  $^{13}\text{C}$  hyperfine coupling constants from the CRENDOR data through diagonalization of the 6 by 6 interaction matrix resulting from a spin  $S = 1$  and  $I = \frac{1}{2}$  system. The hamiltonian describing this system is

$$\mathcal{H} = \beta_e \mathbf{H} \cdot \mathbf{g} \cdot \hat{\mathbf{S}} - (X\hat{S}_x^2 + Y\hat{S}_y^2 + Z\hat{S}_z^2) + \hat{\mathbf{I}} \cdot \mathbf{A} \cdot \hat{\mathbf{S}} - g_n \beta_n \mathbf{H} \cdot \hat{\mathbf{I}}. \quad (14)$$

Finally we note that the difference in CRENDOR transition frequency calculated from a first order and exact treatment of the spin-hamiltonian of eq. (14) for  $1^{13}\text{C-PBQ-}h_4$  amounts to 35 kHz. This is 3.5 times the standard deviation of each measured frequency and therefore exact solution of the energies is preferred.

#### 4. Optically detected EPR, ENDOR and CRENDOR of $1^{13}\text{C-PBQ-}h_4$

In a recent paper [2] we reported the results of an optically detected EPR and proton ENDOR study of  $\text{PBQ-}h_4$  in a  $\text{PBQ-}d_4$  host crystal at 1.8 K. The results showed that the molecule in the excited state is somewhat distorted, into most likely a chair form, and that the unpaired  $n$ -electron density is not completely localized at oxygen. We further reported the unprecedented large effects of mono-deuteration on both the fine-structure parameters and  $g_{zz}$  value of  $\text{PBQ-}h_4$  and explained this as arising from mixing of the lowest inversion levels in the triplet state of  $\text{PBQ-}h_4$  [5,7].

These unusual features of PBQ motivated us to a detailed study of some isotopic species of PBQ and in this paper we report and discuss the magnetic resonance properties of  $1^{13}\text{C-PBQ-}h_4$ , where one of the carbonyl carbons is a carbon-13 nucleus, as guest in a  $\text{PBQ-}d_4$  host crystal at 1.8 K.

In connection with the nuclear spin polarization effects discussed in a previous section, we note here that the hyperfine coupling of the carbon-13 nucleus only

Table 1

Fine-structure parameters and  $g$ -tensor principal values in the lowest triplet state of  $p$ -benzoquinone- $h_4$  [2] and  $1^{13}\text{C-}p$ -benzoquinone- $h_4$  as guests (1 mol%) in  $p$ -benzoquinone- $d_4$  at 1.8 K as obtained from high field optically detected EPR measurements

	$1^{13}\text{C-PBQ-}h_4$	$\text{PBQ-}h_4$
$D$ (MHz)	$-2174 \pm 1.5$	$-2051 \pm 1$
$E$ (MHz)	$115 \pm 1$	$115 \pm 1$
$g_{xx}$	$2.0053 \pm 0.0010$	$2.0045 \pm 0.0005$
$g_{yy}$	$2.0043 \pm 0.0010$	$2.0035 \pm 0.0005$
$g_{zz}$	$2.01026 \pm 0.00010$	$2.00994 \pm 0.00008$

could be obtained by performing next to ENDOR also CRENDOR experiments. In order to extract from these experiments the carbon-13 hyperfine coupling parameters the fine-structure parameters and  $g$ -tensor of  $1^{13}\text{C-PBQ-}h_4$  need to be known. These data were obtained from angular dependent EPR measurements performed and analyzed as previously [2] reported. As in case of  $\text{PBQ-}h_4$  [2] a  $5^\circ$  out-of-plane rotation of the  $y$ -axis of the fine-structure tensor was observed and table 1 contains the fine-structure parameters where for comparison we have also included the analogous data of  $\text{PBQ-}h_4$ .

The increase in the  $|D|$  and  $g_{zz}$  parameter on carbon-13 isotopic substitution only is again surprisingly large and further supports the interpretation of these effects in terms of mixing of molecular [2,5,7] rather than crystal [8] states. The difference in the fine-structure parameter  $|D|$  of the two isotopic species in fact is so large that this allows their separate observation in the CR and LAC effect as is shown in fig. 3.

The carbon-13 hyperfine coupling parameters were obtained by performing ENDOR measurements on the  $|\Delta m_s| = 1$  EPR transitions for the magnetic field in the molecular ( $yz$ ) plane and CRENDOR measurements in a perpendicular ( $xz$ ) plane. For a magnetic field along the molecular  $z$ -axis both ENDOR and CRENDOR transitions could be observed. However a  $5^\circ$  out-of-plane rotation from this axis permitted no longer observation of the ENDOR transitions.

Fig. 4 shows the CRENDOR spectrum obtained for a magnetic field along the molecular  $z$ -axis. The single line at 17.6 MHz is due to a  $^{13}\text{C}$ -nuclear transition and the quadruplet of lines at 6.9 MHz is due to proton nuclear transitions in the  $m_s = 1$  level.

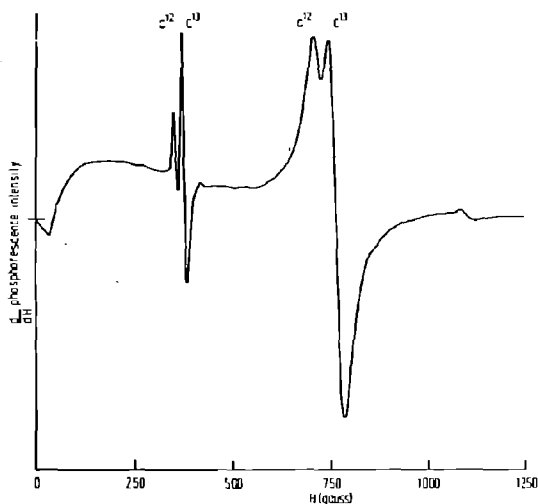


Fig. 3. Cross-relaxation (386 gauss) and level anticross effect (772 gauss) in the phosphorescence of  $1^{13}\text{C}$ -*p*-benzoquinone- $h_4$  at 1.8 K for a magnetic field parallel to the molecular  $z$ -axis. Note the broad underlying cross-relaxation effect at low magnetic field.

The observation of four proton CRENDOR lines shows that the introduction of a single  $^{13}\text{C}$ -nucleus in the carbonyl position leads to an observable loss of molecular (not crystal site) inversion symmetry. The coupling between the electronic and nuclear motions indeed must be very strong!

The angular dependence in the  $xz$  plane of the CR effect and of the carbon-13 CRENDOR difference frequency together with the computer fitted curves is shown in fig. 5.

The angular dependence in the  $yz$  plane of one of the EPR transitions ( $|0\rangle \leftrightarrow |1\rangle$ ) and the carbon-13 ENDOR sum frequency is shown in fig. 6.

The computer fittings of figs. 5 and 6 were obtained as follows: The angular dependence of the EPR effect was used to obtain the data of table 1.

The CR effect was calculated from the data in table 1 and eq. (12) whereby an isotropic  $g_e$  value for the radical was assumed. The CRENDOR transition frequency was least squares fitted to the exact solution of eq. (14) together with the ENDOR transition frequency which was calculated from a first order expression given previously (eq. (5) of ref. [2]).

The carbon-13 hyperfine data obtained from these

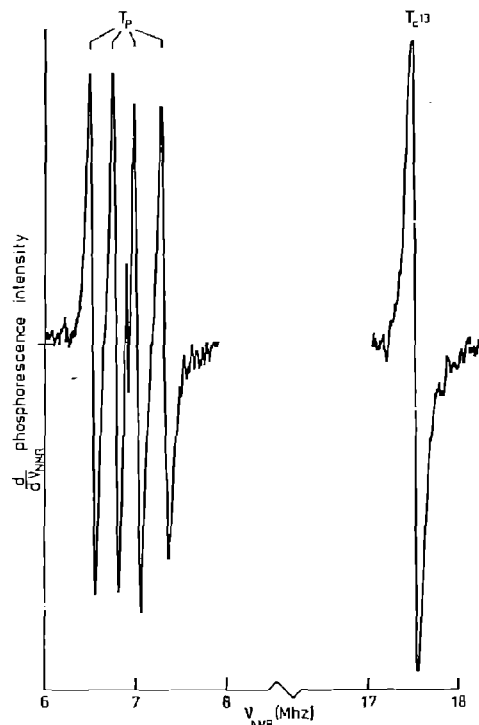


Fig. 4. Optical detection of the nuclear spin alignment at the cross-relaxation field ( $\sim 386$  gauss) (CRENDOR) in the lowest triplet state of  $1^{13}\text{C}$ -*p*-benzoquinone- $h_4$  as guest in *p*-benzoquinone- $d_4$  at 1.8 K. The magnetic field is oriented along the molecular  $z$ -axis of one of the PBQ molecules in the unit cell. The single line ( $T^{13}\text{C}$ ) is due to carbon-13 and the quadruplet ( $T_p$ ) arises from the protons.

results are presented in table 2 and refer to the ground-state molecular axis system [9]. The absolute signs of the hyperfine elements were secured through observation of  $^{13}\text{C}$  ENDOR transitions on both the  $|+1\rangle$  and  $|-1\rangle$  electron spin states while in case of the  $^{13}\text{C}$  CRENDOR transition the electron spin state in which the nuclear transition occurred was known. We further note here that although coincidence of the  $z$ -principal axis of the  $^{13}\text{C}$ -hyperfine tensor with the carbonyl direction of PBQ in the groundstate is demanded by our experiments, a small out-of-plane rotation of the  $y$ -axis would have escaped detection in the present experiment. This is due to the fact that neither ENDOR nor CRENDOR spectra could be obtained for a magnetic field rotation in the  $xy$  molecular plane.

The implication of the alignment of the  $z$ -axis of the

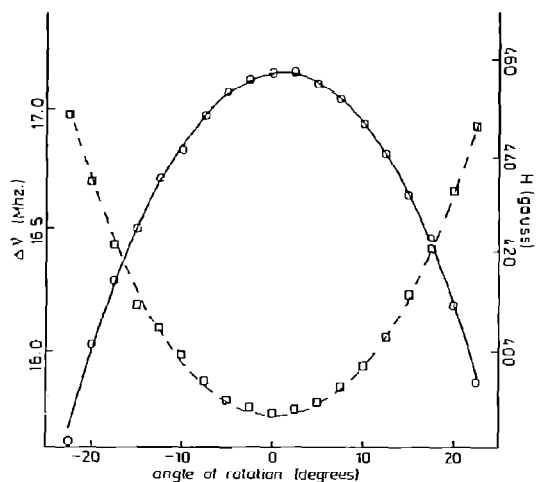


Fig. 5. Angular dependence of the cross-relaxation field (squares) and carbon-13 CRENDOR difference frequency (circles) for the lowest triplet state in  $1\text{-}^{13}\text{C}$ -*p*-benzoquinone- $h_4$  at 1.8 K. The solid lines are computer fittings using the data displayed in tables 1 and 2.  $\Delta\nu$  represents the difference between the measured carbon-13 CRENDOR frequency and the free carbon-13 frequency at the cross-relaxation field. The magnetic field is rotated in the (nearly) *xz* molecular plane and at zero degrees is (nearly) parallel to the long molecular *z*-axis.

Table 2

The carbon-13 hyperfine tensor principle values of the lowest triplet state in  $1\text{-}^{13}\text{C}$ -*p*-benzoquinone- $h_4$  as guest in *p*-benzoquinone- $d_4$  at 1.8 K. The principal axis system of the  $^{13}\text{C}$ -hyperfine tensor coincides (within the accuracy of our measurements) with the ground state molecular axis system. The numbers between parentheses were obtained from ab initio calculations on PBQ [12]

Experimental (MHz)	Isotropic part (MHz)	Anisotropic part (MHz)
$A_{xx} = -2.7$	$A_{\text{iso}} = -11.7$	$A'_{xx} = +9.0$ ( 7.54)
$A_{yy} = -15.15$		$A'_{yy} = -3.5$ (-3.55)
$A_{zz} = -17.26$		$A'_{zz} = -5.5$ (-3.99)

$^{13}\text{C}$ -hyperfine tensor with the groundstate carbonyl direction is that the excited state chairform [2] of PBQ has been reached through only out of plane displacement of the non-carbonyl carbon atoms. Our recently reported [2] proton-ENDOR measurements did not allow such a conclusion. The  $^{13}\text{C}$ -hyperfine tensor elements themselves contain information about the spin-density distribution in the excited state of the molecule.

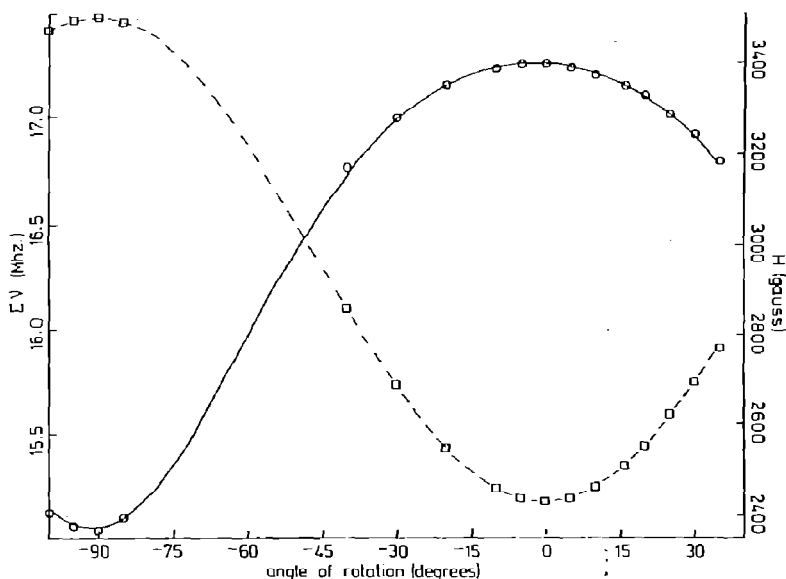


Fig. 6. Angular dependence of the EPR ( $0| \rightarrow | -1\rangle$ ) transition field (squares) and carbon-13 ENDOR sum frequency (circles) for the lowest triplet state in  $1\text{-}^{13}\text{C}$ -*p*-benzoquinone- $h_4$  at 1.8 K. The solid lines are computer fittings using the data displayed in tables 1 and 2.  $\Sigma\nu$  represents the sum of the carbon-13 ENDOR frequency and the free carbon-13 frequency at the EPR transition field studied. The magnetic field is rotated in the (nearly) *yz* molecular plane and at zero degrees is (nearly) parallel to the long molecular *z*-axis.



From the fact that the pure anisotropic  $^{13}\text{C}$ -hyperfine elements are not far from a 2:–1:–1 ratio we conclude that the  $\pi$ -electron spin density residing at the  $^{13}\text{C}$ -nucleus itself is mainly responsible for the anisotropic hyperfine coupling.

For a spin-density of 1 at the  $^{13}\text{C}$ -nucleus the principal hyperfine elements are 128, –64 and –64 MHz [10] and this yields for the  $\pi$ -spin density at the carbonyl carbon ( $\rho_1^\pi$ ) 0.14\*. This is a lower limit for  $\rho_1^\pi$  since the effect of  $n$ -spin density at oxygen will decrease the (absolute) values of the anisotropic hyperfine elements caused by  $\rho_1^\pi$  and therefore  $\rho_1^\pi \geq 0.14$ . Das and Fränkel [11] determined  $\rho_1^\pi$  in the negative ion of PBQ to be between 0.15 and 0.18 depending on the solvent. Our measurements therefore indicate that correlation effects between the  $n$  and  $\pi$  unpaired electrons indeed are small as assumed previously [2]. The non-carbonyl carbon  $\pi$ -spin density in the lowest triplet state of PBQ will therefore be quite close to its value (0.09) in the negative ion.

We then calculate for the  $\pi$ -spin density at oxygen ( $\rho_2^\pi$ )  $\lesssim 0.18$ . This means that in the lowest  $n\pi^*$  triplet state of PBQ the electron excited out of the oxygen lone pair orbital into the  $\pi^*$  orbital is delocalized over the molecule with about equal density at the carbonyl-carbon and oxygen and half this density at the other carbon atoms.

We further note that the sign and magnitude of the isotropic hyperfine coupling constant of the carbon-13 nucleus support this picture.

Using the McConnell type relation employed by Das and Fränkel [11], we calculate for the  $\pi$ -contribution to  $A_{\text{iso}}^{\text{C}}$  in the lowest triplet state of PBQ, with the quoted  $\pi$ -spin densities, –3.7 MHz. Experimentally we find  $A_{\text{iso}}^{\text{C}} = -11.7$  MHz and the difference between these numbers must be primarily due to the polarization effect of the  $n$ -density at oxygen.

We finally wish to mention here that we [12] have used the wave functions obtained from ab-initio calculations on PBQ by Jonkman et al. [13] to calculate the anisotropic hyperfine interaction constants of all nuclei.

In table 2 we have included the numbers calculated for the  $^{13}\text{C}$ -nucleus and the agreement between theory and experiment is seen to be very satisfactory. The calculations and detailed discussion thereof will be presented in a future publication.

\* The total  $\pi$ -spin density is normalized to 1.

## 5. Experimental

$1\text{-}^{13}\text{C-PBQ-}h_4$  was prepared from 90% enriched  $1\text{-}^{13}\text{C}$ -benzoic acid as supplied by Stohler Isotopic Chemicals, Azusa (California) as follows. The  $1\text{-}^{13}\text{C}$ -benzoic acid was first converted into  $1\text{-}^{13}\text{C}$ -aniline as described by Bachman and Goldmacher [14] and Snyder et al. [15] and then oxidized to  $1\text{-}^{13}\text{C-PBQ-}h_4$  following the procedure reported by Willstätter [16]. The isotopically mixed crystals ( $\sim 1$  mol%) of  $1\text{-}^{13}\text{C-PBQ-}h_4$  in  $\text{PBQ-}d_4$  were grown from a Bridgeman furnace and oriented using a polarizing microscope.

Excitation of the PBQ mixed crystal was done using a Philips Cs 200 Watt Mercury arc instead of a Xenon source employed previously. The advantage of the mercury arc is that we obtain comparable signal to noise ratio in our experiments while less heating the sample. The concentration of the photochemically produced radicals was optimized by exciting the crystal at 4.2 K for about 5 minutes with the unfiltered output of the excitation source.

For further details on detection of EPR, ENDOR and CRENDOR ref. [2] should be consulted.

## 6. Summary and conclusions

This paper shows that at low temperature cross-relaxation between a radical and a triplet state excited molecule can produce a high degree of nuclear spin polarization in the molecule.

The prerequisite for such nuclear alignment is formulated and it is also shown that the exact degree of nuclear polarization can be calculated if the populating and decay rates of the individual spin sublevels are known.

The possibility of optical detection of this nuclear spin polarization (CRENDOR) is also examined and found only to be feasible for the least radiative electron spin sublevel.

The paper further contains report of the fine-structure and  $g$ -tensor and  $^{13}\text{C}$ -hyperfine coupling parameters of  $1\text{-}^{13}\text{C-}p$ -benzoquinone- $h_4$  in its lowest triplet state, which were obtained through optical detection of EPR, ENDOR and CRENDOR transitions at 1.8 K.

From the  $^{13}\text{C}$ -hyperfine data it was concluded that in the lowest triplet state of  $p$ -benzoquinone the  $\pi$ -electron spin density distribution is such that the carbonyl carbon and oxygen carry about equal density while the

non-carbonyl carbons each carry approximately half this density.

### Acknowledgement

We are indebted to Berend Kwant for the synthesis of 1-<sup>13</sup>C-*p*-benzoquinone-*h*<sub>4</sub> and to L. Benthem and W. Zandvoort for help in some of the experiments.

### References

- [1] D. Stehlik, A. Doehring, J.P. Colpa, E. Callaghan and S. Kesmarky, *Chem. Phys.* 7 (1975) 165, and references therein.
- [2] J.H. Lichtenbelt, J.G.F.M. Fremeijer, H. Veenliet and D.A. Wiersma, *Chem. Phys.* 10 (1975) 107.
- [3] W.S. Veeman and J.H. van der Waals, *Chem. Phys. Lett.* 7 (1970) 65.
- [4] W.S. Veeman, A.L.J. van der Poel and J.H. van der Waals, *Mol. Phys.* 29 (1975) 225.
- [5] H. Veenliet and D.A. Wiersma, *Chem. Phys.* 8 (1975) 432.
- [6] C.A. Hutchison and G.A. Pearson, *J. Chem. Phys.* 43 (1965) 2545; 47 (1967) 520.
- [7] H. Veenliet and D.A. Wiersma, *Chem. Phys. Lett.* 33 (1975) 305.
- [8] B.H. Loo and A.H. Francis, to be published.
- [9] J. Trotter, *Acta Cryst.* 13 (1960) 86.
- [10] W.V. Smith, P.P. Sorokin, I.L. Gelles and G.J. Lascher, *Phys. Rev.* 115 (1959) 1546.
- [11] M.R. Das and G.K. Fraenkel, *J. Chem. Phys.* 42 (1965) 1350.
- [12] J.H. Lichtenbelt, D.A. Wiersma, H.T. Jonkman and G.A. van der Velden, to be published.
- [13] H.T. Jonkman, G.A. van der Velde and W.C. Nieuwpoort, *Quantum Chemistry – The State of the Art, Proceedings of S.R.C. Atlas Symposium, No. 4 (1974)* p. 243.
- [14] G.B. Bachman and J.E. Goldmacher, *J. Org. Chem.* 29 (1964) 2576.
- [15] H.R. Snijder, C.T. Elstom and D.B. Kellom, *J. Am. Chem. Soc.* 75 (1953) 2014.
- [16] R. Willstätter and S. Dorogi, *Ber.* 42 (1939) 2147.